Destabilization of the LiNH₂−LiH hydrogen storage system by aluminum incorporation

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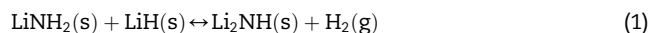
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ABSTRACT

The lithium amide−lithium hydride system ($LiNH_2$−LiH) is one of the most attractive light-weight materials for hydrogen storage. In an effort to improve its hydrogen sorption kinetics, the effect of 1 mol% $AlCl_3$ addition to $LiNH_2$−LiH system was systematically investigated by differential scanning calorimetry, X-ray diffraction, Fourier transform infrared analysis and hydrogen volumetric measurements. It is shown that Al^{3+} is incorporated into the $LiNH_2$ structure by partial substitution of Li^+ forming a new amide in the Li−Al−N−H system, which is reversible under hydriding/dehydriding cycles. This new substituted amide displays improved hydrogen storage properties with respect to $LiNH_2$−LiH. In fact, a stable hydrogen storage capacity of about 4.5−5.0 wt% is observed under cycling and is completely desorbed in 30 min at 275 °C for the Li−Al−N−H system. Moreover, the concurrent incorporation of Al^{3+} and the presence of LiH are effective for mitigating the ammonia release. The results reveal a common reaction pathway for $LiNH_2$−LiH and $LiNH_2$−LiH plus 1 mol% $AlCl_3$ systems, but the thermodynamic properties are changed by the inclusion of Al^{3+} in the $LiNH_2$ structure. These findings have important implications for tailoring the properties of the Li−N−H system.

1. Introduction

Light metal hydrides or complex hydrides constitute highly desirable materials for hydrogen storage due to their large volumetric hydrogen densities, greater than those obtained in the liquid state, and gravimetric storage densities that exceed DOE targets. Among complex hydrides, the two-component reactive hydride mixture formed from $LiNH_2$ and LiH displays many relevant features. These include reversibility, relatively low operation temperature and low cost. In fact, since the influential paper by Chen et al. in 2002 [1], lithium amide ($LiNH_2$) has been extensively studied as a promising material for hydrogen storage. Hydrogen release occurs in the $LiNH_2$−LiH mixture *via* a reversible solid state decomposition reaction into lithium imide (Li_2NH) and hydrogen:

$$LiNH_2(s) + LiH(s) \leftrightarrow Li_2NH(s) + H_2(g) \qquad (1)$$

Reaction (1) theoretical release is 6.5 wt% of hydrogen, with a calculated reaction enthalpy of −44.5 kJ/mol H_2 [1,2].

However, further measurements [3,4] have suggested higher values (about −66 kJ/mol H_2) than the previous estimate.

Concerning the mechanism of Reaction (1), Chen et al. have suggested that the dehydriding proceeds *via* direct interaction between solid-phases, which is driven by the exothermic reaction between the positively charged H^+ from $LiNH_2$ and the negatively charged H^- from LiH [1,2]. On the other hand, two independent studies [5,6] have provided strong evidence that Reaction (1) proceeds with the following two elementary reactions ("ammonia mediated mechanism"):

$$2LiNH_2(s) \rightarrow Li_2NH(s) + NH_3(g) \qquad (2)$$

$$NH_3(g) + LiH(s) \leftrightarrow LiNH_2(s) + H_2(g) \qquad (3)$$
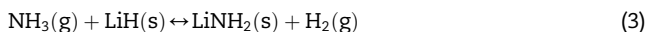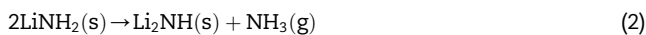
First, $LiNH_2$ decomposes releasing NH_3, which subsequently reacts with LiH to form $LiNH_2$ again and liberates hydrogen. Reaction (3) has shown to be ultrafast and exothermic, leading to full consumption of NH_3 by LiH in the order of microseconds [5,6]. In contrast, using pure $LiNH_2$ as starting material, it has been shown that Reaction (2) is diffusion-controlled and proceeds in minutes [7]. A further study developed by Shaw and co-workers has revealed that the dehydrogenation of the $LiNH_2$–LiH mixture is diffusion-controlled and the rate-limiting step is NH_3 diffusion through the Li_2NH product layer outside the $LiNH_2$ shrinking core [8]. Due to the continued dehydrogenation/hydrogenation cycles, the reaction would involve repeated nucleation of the solid phases and continuous flaking-off of the $LiNH_2$ layer formed at the surface of LiH after reacting with NH_3. An independent investigation has proposed that the dehydrogenation mechanism for Li−N−H takes place through a heterogeneous solid-state reaction controlled by the diffusion of Li^+ and H^- from LiH and $LiNH_2$ with the formation of $Li_2NH_2^+$ as an intermediate state [9]. The results support the hypothesis of a direct solid-state reaction between $LiNH_2$ and LiH, rather than an ammonia-mediated route. The only condition is that the reactants comprise uniformly mixed small particles to ensure direct and frequent contacts. Quite recently, David et al. [10] have proposed a more detailed ion migration model based on the observed non-stoichiometric bulk reaction in the Li_2NH−$LiNH_2$ system, which takes place through the evolution of NH_3. It is suggested that the dehydriding/hydriding performances are highly dependent on the mobility of Li^+ and H^+ ions; dehydrogenation would occur once Li^+ has moved to adjacent vacant tetrahedral sites within the $LiNH_2$ structure creating a Frenkel defect pair. One crucial implication of this mechanism is that an improved hydrogen sorption performance of the Li−N−H system can be expected when increasing the Li^+ mobility by creating a defective structure.

Many attempts have been made to enhance the hydrogen sorption properties of the $LiNH_2$−LiH system, with the main focus on its high desorption temperature and slow reaction kinetics [9,11−17]. Usually three main approaches have been applied to enhance the hydrogen sorption performance of the $LiNH_2$−LiH composite. The first one is the application of ball milling to reduce particle size and facilitate the contact between the reactants [11,12]. The second approach involves the addition of potential catalysts to reduce the desorption temperature [13,17]. The last strategy is focused on the destabilization of the N−H bond by introducing dopants of higher

electronegativity than Li [18,19]. Nakamori and Orimo were pioneering in this last approach, where the introduction of a dopant such as Mg provides a route for the synthesis of new families of complex imides/amides and other composite systems [18,19]. A secondary effect of these doped materials might be the introduction of defects in order to maintain charge balance, which could modify the Li^+ mobility.

Some of these approaches were first adopted by Ichikawa et al. [11]. In this initial investigations 1 mol% of Ni, Fe, Co and $TiCl_3$ were added to the $LiNH_2$−LiH system and thermal desorption mass spectroscopy was used to follow the hydrogen desorption behavior. In ball milled mixtures without catalysts, Ichikawa et al. [11,12] observed that ammonia evolution was reduced significantly compared to samples mixed manually. In addition, when the catalysts were added by milling, both NH_3 emission and hydrogen desorption temperature were significantly reduced. The effect was most prominent for $TiCl_3$, where 5.5 wt% of hydrogen was released between 150 and 250 °C, with an activation energy of 110 kJ/mol. Later studies [13] revealed that nanoparticles of Ti or TiO_2 were also effective in reducing the desorption temperature. It was suggested that $TiCl_3$ and TiO_2 react with LiH in the ball milled mixture to produce the corresponding LiCl or Li_2O plus Ti nanoparticles; no activation energies of catalyzed and non-catalyzed materials were reported. These dispersed catalysts were characterized by X-ray absorption spectroscopy [14], indicating that Ti atoms in the titanium compounds have a common chemical bonding. Yao et al. showed that the addition of Mn, V and their oxides to pure $LiNH_2$ reduce its decomposition temperature [15]. However, when these additives are mixed with $LiNH_2$ plus LiH, no discernable effect on the hydrogen desorption kinetics or desorption temperature is observed. From these results, they concluded that the rate-limiting step for dehydrogenation from $LiNH_2$−LiH was the reaction between LiH and NH_3. Matsumoto et al. showed the beneficial effect of milling time on the hydrogen desorption kinetics of the $LiNH_2$−LiH mixture with $TiCl_3$ as catalyst [16]. The activation energy estimated for the Li−N−H system with catalyst was similar to that of Ichikawa et al., but the activation energy of the pristine sample showed a much smaller value of 54 kJ/mol. In a recent work, Isobe et al. analyzed the catalytic role of $TiCl_3$ using X-ray absorption spectroscopy measurements [17]. The results indicate that the Ti atoms in the Ti compounds have a common electronic state, in particular agrees with that of $TiCl_3.5NH_3$. This compound may show catalytic effect in the ammonia mediated reaction, playing a role as a kind of ammonia carrier. Additionally, the kinetics of the Li−N−H system was improved by BN addition [9]. It was suggested that BN improves the mass transport between the two reactants and thus enhances the overall hydrogen desorption kinetics in the heterogeneous solid state reaction between $LiNH_2$ and LiH.

However, from the previous works, it is not clear how titanium (or other catalyst) affects the bulk of the amide catalytically and keeps this role during hydrogen cycling. Motivated by these facts as well as by the ion migration model, we mechanically prepared a $LiNH_2$−LiH composite with 1 mol% $AlCl_3$ addition and investigated their hydrogen storage properties by comparing with $LiNH_2$−LiH. The improved hydrogen sorption properties observed were associated with the